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THE REMOVAL OF CLAY AND SILICA FROM WATER¹

BY OTTO M. SMITH²

Silica is found in natural waters in two forms, the one insoluble and the other soluble. In the latter it is usually known as silicic acid and is reported as SiO_2 in the ordinary water analyses. In solution it occurs in a colloidal form or in combination with the basic elements. Its presence in water used for steam purposes has always been considered as detrimental and conducive to the formation of a hard flinty scale. Silicic acid is said to be responsible for many boiler disturbances. When the acid is distilled with water solutions of nitrates and chlorides, nitric and hydrochloric acid are liberated.

Turbidity in water is generally caused by the suspensions of very finely divided mineral matter, mainly clay. Clay may be defined as a mixture of minerals of which the most representative members are the silicates of aluminum, iron, and the alkalies, and the alkaline earths and organic substances. The hydrated aluminum silicate or kaolin ($\text{Al}_2\text{O}_3, 2\text{SiO}_2, 2\text{H}_2\text{O}$) is the most abundant compound.

There are many instances in the literature emphasizing the difficulties of clarifying water containing finely dispersed clay particles. Fuller³ and Ellms⁴ found that at times there occurred a turbidity in the Ohio River that was difficult to coagulate and required an abnormal consumption of alum. Black and Veatch⁵ and Catlett⁶ show the difficulties in the treatment of such water.

Properties of colloids. As silicic acid and a clay suspension are considered to be present in water in a colloidal form, a brief discussion of the general properties of colloids will be desirable. Burton defines a colloid solution as

¹ Read before the Illinois Section, March 25, 1919. Discussion of this paper is requested, and should be sent to the Editor.

² Chemist, Procter & Gamble Company, Ivorydale, Ohio.

³ "Water Purification at Louisville, Ky."

⁴ *Engineering Record*, 51, 552 (1905).

⁵ *Engineering Record*, 72, 292.

⁶ *Engineering Record*, 73, 741.

A suspension, in a liquid medium, of fine particles which may be graded down from those of microscopic to those of molecular dimensions; the one property common to all such solutions is that the suspended matter will remain almost indefinitely in suspension in the liquid, generally in spite of rather wide variations in temperature and pressure; the natural tendency to settle, due to the attraction of gravitation, is overbalanced by some other force tending to keep the small masses in suspension.

It is possible to show that there is a continuous gradation in the size of particles from those invisible to those of microscopic dimensions and this leads to the belief that there is a gradation in size from the smallest of these to that of molecules. Small microscopic objects have a continuous movement known as the Brownian movement. If to a suspension of clay increasing amounts of alum be added, there is a gradual cessation of this movement, a clumping together of the particles and finally coagulation and precipitation. At the point of precipitation there is no Brownian movement.

If a beam of light be passed through a dust-laden air, the dust particles become luminous and visible to the eye. Likewise if light rays be passed through a perfectly clear solution of colloidal iron or silicic acid, the minute particles will reflect light and the solution appear turbid. If the colloid is coagulated and allowed to settle, the solution no longer appears turbid. This phenomenon is known as the Tyndall effect and is shown in figure 1. In this photograph both bottles contained a solution of colloidal iron, but the one on the right was coagulated by the addition of tap water several hours prior to the taking of the picture. Projecting through each bottle are four beams of light but only in the one containing the uncoagulated iron colloid are they visible; in the other there are no particles to reflect the light rays. Figure 2 shows that a solution of colloidal iron is clear although dark in color.

These tiny invisible particles which will pass through the pores of ordinary filter paper, carry electrical charges and will move towards the positive or negative pole when subjected to an electric current. Iron and aluminum hydroxides are positive and clay and silicic acid negative. In dealing with negatively charged particles the most active coagulants are the trivalent cations, aluminum and iron, next the bivalent cations, calcium and magnesium, and lastly univalent cations of sodium, potassium and hydrogen.

If a small amount of alum be dissolved in a large amount of water containing carbonate or bicarbonate, there is a reaction in which

the aluminum of the alum passes from an ionic state into probably colloidal condition as aluminum hydroxide, and then into an insoluble gelatinous form commonly referred to as "floc" by the water works operator. If increasing amounts of colloidal aluminum hydroxide or alum be added to clay in suspension there is a diminution in the charge on the clay particles, then neutralization followed by

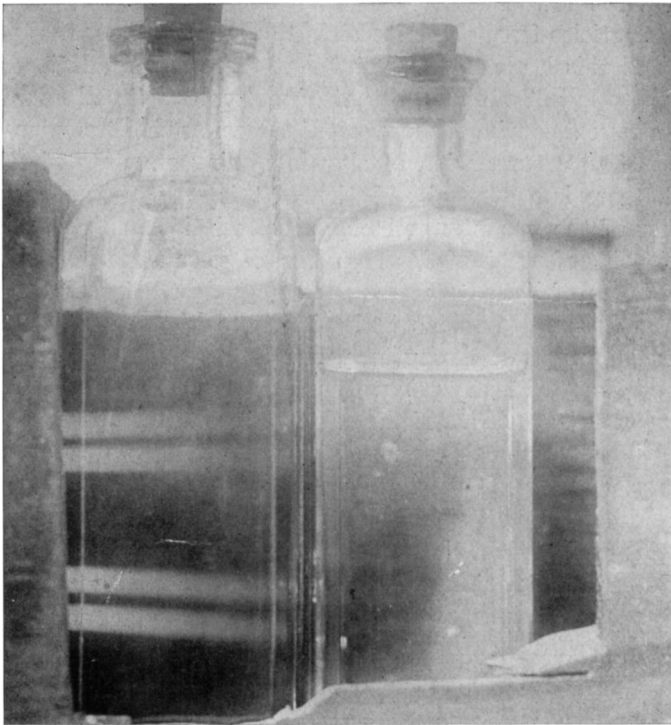


FIG. 1. TYNDALL EFFECT PRODUCED BY COLLOIDAL IRON AND ABSENCE OF THIS EFFECT WHEN COAGULATED AND SETTLED.

coagulation, and when an excess is added a reversal in the sign of the charge on the colloidal material.

Another property of colloids which is quite important is their power of absorbing colloids and fine particles such as bacteria, clay, coloring materials, etc. It is this property of the slime on the sand in filters and on the stones in contact beds, that results in the purification of the liquid passing through them.

Coagulation of clay suspensions. In water purification, the aim is the removal of a very small amount of clay or silica from a large amount of water. It is clearly evident from a study of dilute clay

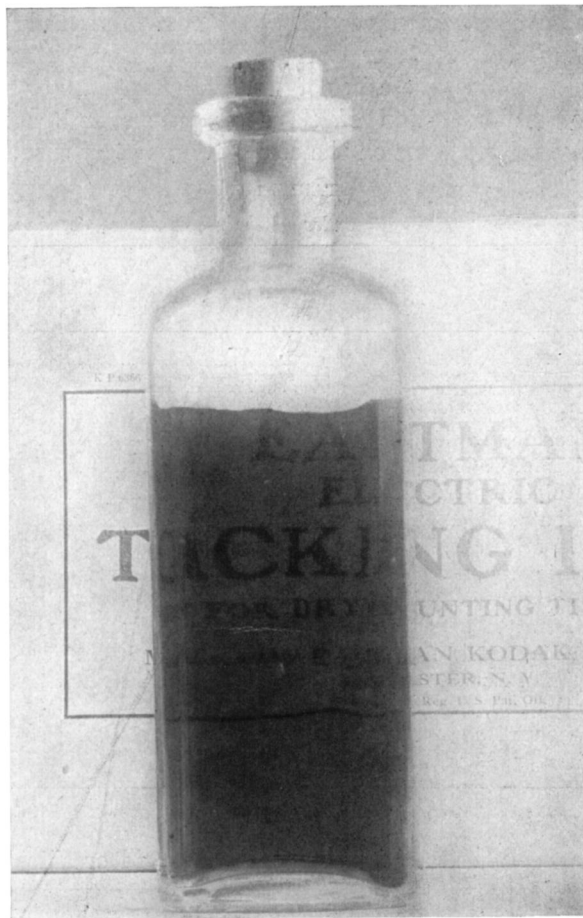


FIG. 2. PHOTOGRAPH OF PRINTING TAKEN THROUGH A COLLOIDAL SOLUTION OF IRON.

suspensions and colloidal silicic acid that the physical state of the substances and their chemical properties must be taken into consideration and the factors which influence them, i.e. (1) degree of dispersion, (2) the presence of the protective colloids and absorbed

substances, (3) magnitude and kind of electric charge, (4) the liquid or dispersing medium, (5) the ionic content of the liquid, (6) the concentration, (7) the temperature, and (8) the speed of reaction of added substances.

In discussing experiments which were conducted in the laboratories of the Illinois State Water Survey Division, the author will endeavor to show, first, the effect of various electrolytes or salts upon the rate of sedimentation of clay suspensions and, second, the effect of these electrolytes on the coagulation of clay suspensions by

TABLE 1

Electrolytes arranged in the order of their efficiencies as coagulants

ELECTROLYTE	1 MILLIGRAM EQUIVALENT EX- RESSED IN PARTS PER MILLION
Aluminum sulphate (alum) (17 per cent Al).....	52.9
Ferrous sulphate, $\text{FeSO}_4, 7\text{H}_2\text{O}$	139.0
Calcium hydroxide (hydrated lime) CaOH	37.0
Barium hydroxide, $\text{Ba}(\text{OH})_2$	85.8
Calcium chloride, CaCl_2	55.5
Magnesium sulphate, MgSO_4	60.2
Calcium sulphate, CaSO_4	68.0
Magnesium bicarbonate, $\text{Mg}(\text{HCO}_3)_2$	73.2
Calcium bicarbonate, $\text{Ca}(\text{HCO}_3)_2$	81.0
Magnesium carbonate, MgCO_3^*	42.2
Calcium carbonate, CaCO_3^*	50.0
Sodium chloride, NaCl	58.5
Sodium sulphate, Na_2SO_4	71.0
Sodium bicarbonate, NaHCO_3	84.0
Sodium carbonate Na_2CO_3	106.0
Sodium hydroxide, NaOH	40.0

*This salt has little effect because of its low solubility

alum in the presence and absence of silicic acid or silicates. Suspensions of Tennessee ball clay were used, having turbidities of 400 and 420 parts per million and coefficients of fineness of 0.81 and 0.79. Reagents were added to 100-cc. portions of the suspension and thoroughly mixed by shaking one minute. The sample was then allowed to remain perfectly quiet and the turbidity determined at a point $\frac{1}{2}$ inch below the surface at appropriate intervals of time. The electrolytes used are arranged in the order of their efficiencies as coagulants, when present in concentrations shown. At this point it might be well to state that the same reagent at one concentration

may disperse the suspended materials, thus preventing them from settling, and at another concentration cause the particles to collect together, producing coagulation.

The quantities of chemical used are expressed in milligram equivalents instead of parts per million because this is the most logical method of comparing chemical activity. An equivalent weight may be defined as the quantity of the radical or ion which combines with or will displace eight parts of oxygen; a milligram equivalent is one one-thousandth of one equivalent. One milligram per 1000 cc. of water is equivalent to one part per million. Table I shows the value of 1 mgm. equivalent of the various electrolytes in parts per million.

The salts arranged according to their efficiencies as coagulants are aluminum sulphate, ferrous sulphate, calcium and barium hydroxides, calcium chloride, magnesium and calcium sulphate, magnesium and calcium bicarbonate. The coagulating powers of calcium and barium hydroxide are practically the same and the ratio of the coagulating powers of aluminum to that of these ions is about five to one (see figs. 3 and 4). Sodium chloride has little effect until its concentration becomes large. Acid has little effect up to a concentration of 0.35 mgm. equivalent but higher amounts will coagulate. Sodium hydroxide, carbonate, acid carbonate and sulphate have at first a stabilizing influence followed by a coagulating effect, the hydroxide showing this action the greatest and the sulphate the least (fig. 4). When clay suspensions containing the above mentioned electrolytes are coagulated with alum, we find that salts of calcium and barium aid coagulation, while those that disperse, sodium bicarbonate, carbonate, sulphate and hydroxide, retard coagulation (fig. 5). With a given sodium hydroxide content and the addition of graded amounts of alum, there is first dispersion, then coagulation followed by a second dispersion phase (not as stable as the first) and finally coagulation (see fig. 6). As the content of sodium hydroxide is increased, additional amounts of aluminum sulphate must be added in order to produce coagulation and to combat the dispersive power of the hydroxide or sodium compound.

The concentration of chemicals necessary to produce coagulation does not vary with the alkalinity of the solution but seems to be a function of the concentration of hydroxyl ions (obtained from lime or carbonates) and alkali metal (sodium and potassium) ions as well as the cations and their valencies. A water containing large amounts

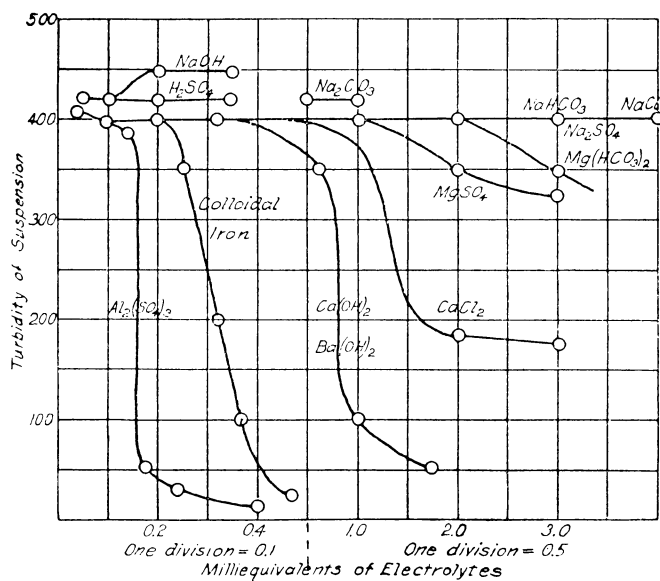


FIG. 3. EFFECT OF ELECTROLYTES ON THE COAGULATION AND SETTLING OF CLAY SUSPENSIONS. SETTLED 1 HOUR.

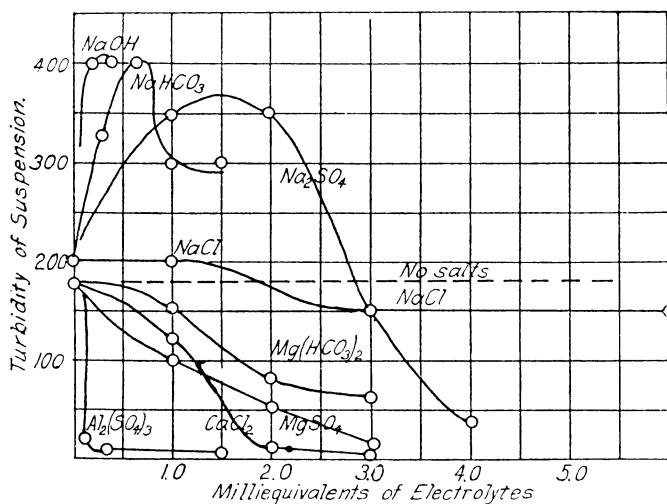


FIG. 4. EFFECT OF ELECTROLYTES ON THE COAGULATION AND SETTLING OF CLAY SUSPENSION. SETTLED 14 HOURS.

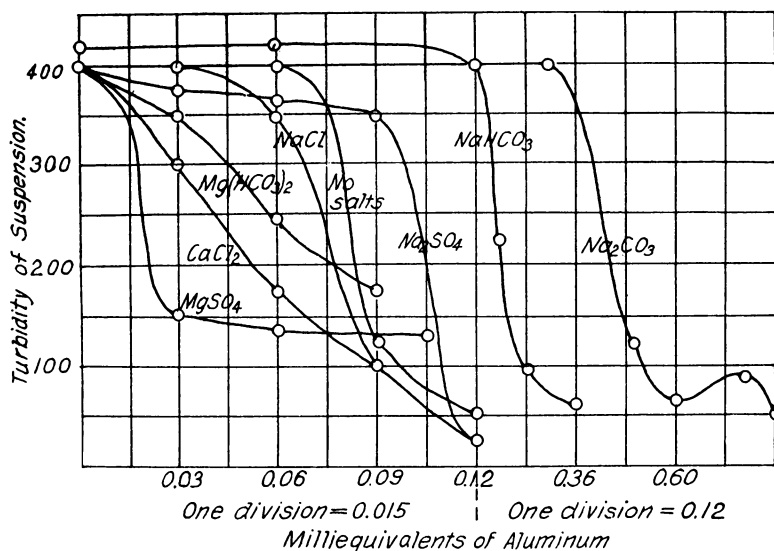


FIG. 5. EFFECT OF ADDING 1 MILLIEQUIVALENT OF ELECTROLYTES ON THE COAGULATION OF CLAY SUSPENSION BY $\text{Al}_2(\text{SO}_4)_3$. SETTLED $1\frac{1}{2}$ HOURS.

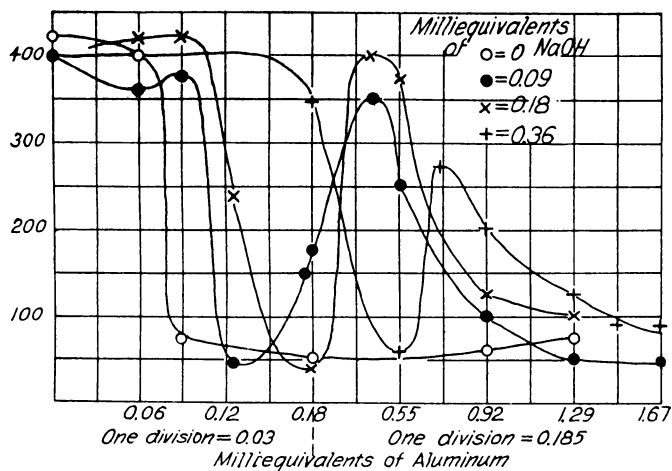


FIG. 6. EFFECT OF NaOH ON THE COAGULATION OF A CLAY SUSPENSION BY $\text{Al}_2(\text{SO}_4)_3$. SETTLED $1\frac{1}{2}$ HOURS.

of sodium salts except sodium chloride and a very small amount of calcium or magnesium salts is much more difficult to clarify than one wherein the magnitude of the concentrations is reversed.

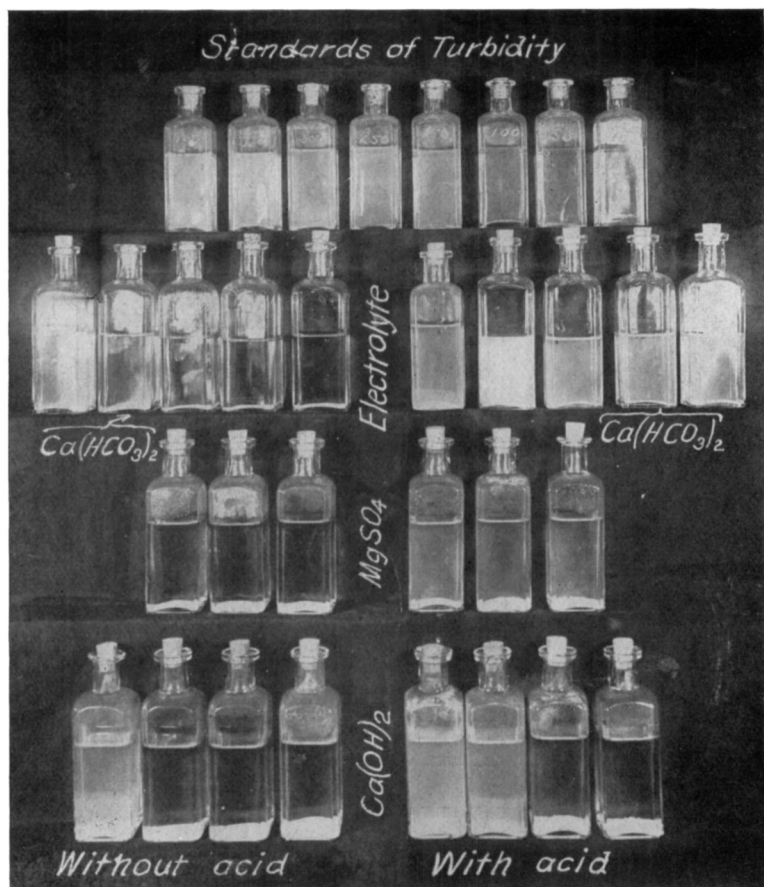


FIG. 7. EFFECT OF COLLOIDAL SILICIC ACID ON THE COAGULATION OF CLAY SUSPENSIONS BY $\text{Al}_2(\text{SO}_4)_3$.

Now when silicic acid is present the effect is very similar to that produced by the sodium compounds and in all cases more alum is needed to produce clarification than is used when the silica colloid is absent. Figures 7 and 8, taken five days after the addition of alum, show this well. To those samples on the right were added 62

parts per million of SiO_2 , and to those on the left none. These solutions were coagulated by the addition of increasing amounts of aluminum sulphate so proportioned that at one end of the series the suspension was partially coagulated and at the other completely clarified; the amounts of aluminum sulphate though varying

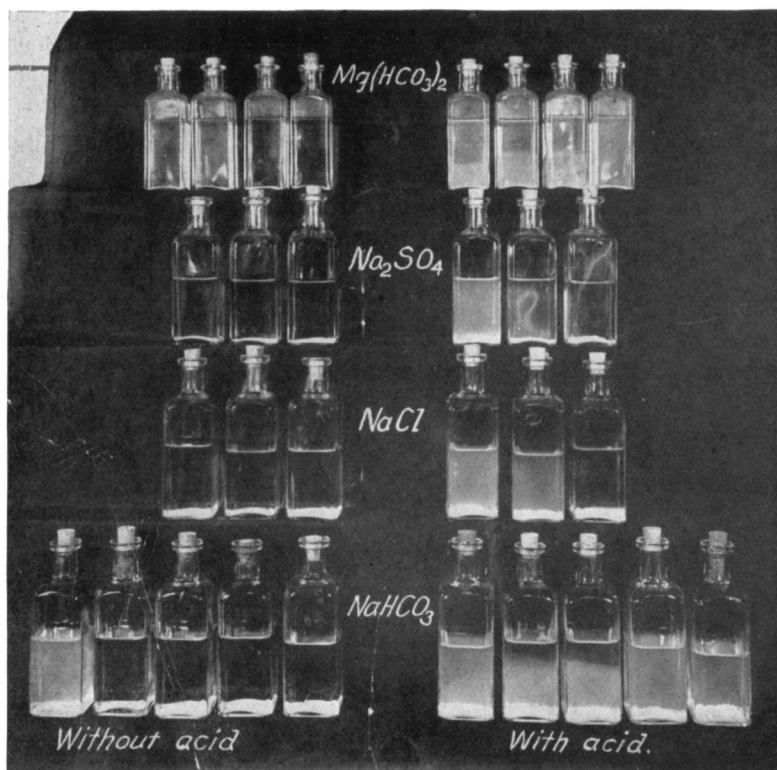


FIG. 8. EFFECT OF COLLOIDAL SILICIC ACID ON THE COAGULATION OF CLAY SUSPENSIONS BY $\text{Al}_2(\text{SO}_4)_3$.

with the different salts are the same in any particular salt. In general the amount of aluminum required to coagulate, per unit amount of silicic acid present, is proportionally larger at low than high concentration. Colloidal silicic acid does not seem to stabilize or disperse the clay suspensoid nor does it influence the rate of sedimentation; in this respect it differs from the alkalis.

Experiments on removing silicic acid showed that it is most efficiently precipitated from solution by the trivalent ions of aluminum and iron, next the bivalent calcium, magnesium and barium, and not precipitated by the univalent sodium and potassium except at very high concentrations. Also that the maximum removal of silicic acid by aluminum hydroxide occurs when the water contains a concentration of hydrogen ion of 1×10^{-8} grams of hydrogen per liter; at this concentration a bright cherry red color is produced when phenolphthalein is added.

Applications. Thus the proper treatment for the removal of colloidal silicic acid is to slightly over-soften with lime and to coagulate

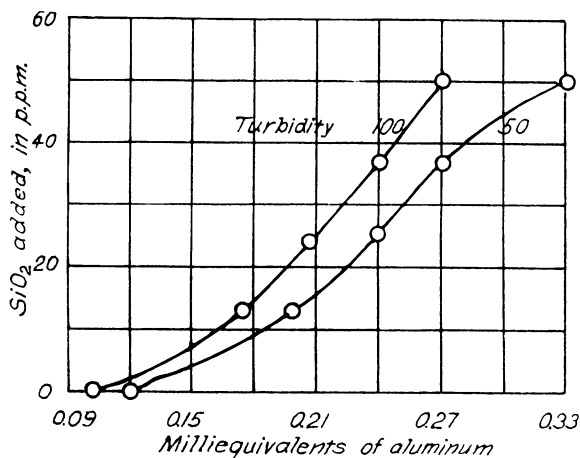


FIG. 9. ALUMINUM NECESSARY TO PRODUCE A DEFINITE CLARIFICATION IN THE PRESENCE OF SILICIC ACID. SETTLED 1 HOUR.

with alum, adding the latter in the form of a dilute solution. Silicic acid can be easily removed from a water containing a high proportion of calcium and magnesium to sodium and the difficulty increases as the amounts of sodium sulphate, carbonate and bicarbonate become larger.

In the coagulation of water containing colloidal clay, the stability of a clay suspension seems to be intimately related to concentration of sodium and potassium, carbonate and sulphate. The amount of alum will be greater the larger the concentration of these and less as the ratio of $\text{Ca} + \text{Mg}$ to Na increases. As the silicic acid increases more alum is required. At a concentration of 20 parts per

million from 0.8 to 1.6 parts per million of alum per 10 parts of SiO_2 are required to combat the influence of the silicic acid (fig. 9).

Waters containing bivalent ions when treated with alum give a sharp abrupt reaction, an increase of 2.6 parts per million of alum coagulates, but when silicic acid or alkalies are present, other factors being constant, a much larger amount of alum is necessary to produce the same clarification and the abruptness of the reaction becomes less as the amount of the silicic acid and alkalies approaches a certain maximum, where the magnitude of the change produced per unit amount of alum is much smaller than in the former case. This phenomenon is exactly similar to that which occurs when

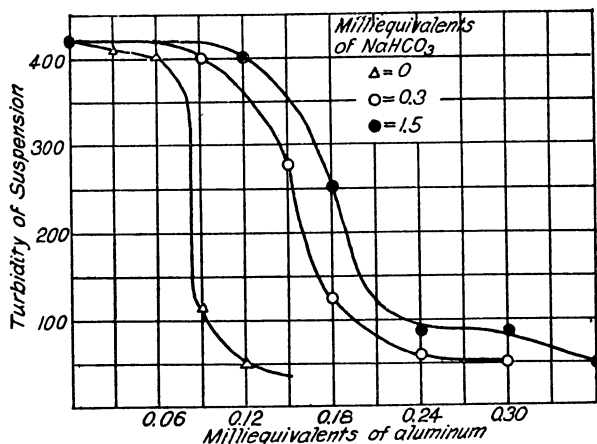


FIG. 10. EFFECT OF NaHCO_3 ON THE COAGULATION OF CLAY SUSPENSION BY $\text{Al}_2(\text{SO}_4)_3$. SETTLED $1\frac{1}{2}$ HOURS.

“colloidal waters” are coagulated by alum and lime. It is this slowness of reactions that misleads many operators into the pitfalls of undertreating this class of waters. In figure 10 the alum required to coagulate was 6.5 parts per million but in the presence of 25 parts per million of sodium bicarbonate 13 parts per million was added before coagulation started. These experiments justify the addition of an excess of calcium hydroxide and allowing it to react with the material in the water for some time, 6 to 12 hours before the addition of alum or ferrous sulphate. This procedure has been effective in purification of water from the Arkansas River at Little Rock, Arkansas, when the suspended material is in a colloidal condition.

In this case river water containing a turbidity due to colloidal material of 200 to 600 parts per million and an alkalinity near 100 was effectively handled by dosing with lime (3 to 4 grains per gallon) until there was an alkalinity to phenolphthalein of 30 to 40 parts per million (a cherry red color) and a methyl orange alkalinity of 60 to 80 parts per million. This water was passed through a sedimentation basin of six to twelve hours retention period, in which some sedimentation resulted, and was then coagulated with about 1 grain of alum or ferrous sulphate. When treated in the regular manner the water was passed through this sedimentation basin, and 5 to 6 grains per gallon of alum and 2 to 3 grains of lime added before coagulation were effective. Even with this large amount of coagulant the water was in very poor condition to filter, while in the former case the water was clear and contained large and well formed flocs, but of course there was an alkalinity to phenolphthalein of 10 to 20 parts per million in the finished waters.